3510 *Inorg. Chem.* **1984**, *23*, 3510–3514

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

EPR Study of $[Co^{II}L_2]^{2+}$, $[Co^{II}LL']^{2+}$, and $[Co^{III}LL'O_2^-]^{2+}$ (L = 2,2′,2″-Terpyridine; L′ = 2,2′-Bipyridine) Complexes in Zeolite Y

KOICHI MIZUNO, SEIICHIRO IMAMURA, and JACK H. LUNSFORD*

Received October 12, 1983

Cobalt(II) ions in zeolite Y react with 2,2′,2″-terpyridine to form low-spin paramagnetic $[Co^{II}(terpy)_2]^{2+}$ complexes. When 2,2′,2″-terpyridine and 2,2′-bipyridine are simultaneously present, both the bis(terpyridine) complex and the mixed-ligand $[Co^{II}(bpy)(terpy)]^{2+}$ complex are formed. In the presence of 30 torr of O_2 the five-coordinate mixed-ligand complex is transformed into the oxygen adduct $[Co^{III}(bpy)(terpy)O_2^-]^{2+}$. The formation of the oxygen adduct is completely reversible at 298 K, and the complex is thermally stable in the presence of oxygen up to 343 K. Preadsorption of water inhibits the formation of the complex, presumably due to competition for the sixth coordination site on the cobalt.

Introduction

Cobalt dioxygen complexes have received considerable attention because of their role as model compounds for oxygen carriers in biological systems and because of renewed interest in separating oxygen from air with a minimum expenditure of energy.[1] In solution both mononuclear and binuclear complexes occur, although the latter are more common, and one often has to use rather bulky ligands to retain the mononuclear form. Some success has been achieved in maintaining mononuclear complexes by immobilizing the complexes either on an ion-exchange resin or in a zeolite.[2-5] Cobalt complexes with ligands such as ammonia, alkylamines and ethylenediamine have been synthesized within the large (13-Å diameter) cavities of zeolite Y. Provided at least one coordination site remains open, the oxygen adduct will form.

Repeated, reversible oxygen adduct formation is required for the use of these complexes in separation processes. This application has been restricted because the complexed oxygen, which may be viwed as a superoxide ion, slowly attacks the ligand. A motivation for this research was to synthesize a cobalt dioxygen complex with sufficiently robust ligands so that they could withstand attack by the complexed oxygen at normal temperatures. The oxygen adduct of the mixed-ligand bipyridine–terpyridine complex in zeolite Y was found to be stable in zeolite Y at temperatures less than 343 K. Dinuclear cobalt complexes involving bipyridine and terpyridine ligands have been observed in aqueous solution by Huchital and Martell,[6] but the mononuclear oxygen adduct has not been previously reported.

In the course of this study both the $[Co^{II}(terpy)_2]^{2+}$ and the $[Co^{II}(bpy)(terpy)]^{2+}$ (bpy = 2,2′bipyridine; terpy = 2,2′,2″-terpyridine) complexes also were synthesized within zeolite Y and characterized by EPR spectroscopy. The related complex $[Co^{II}(bpy)_3]^{2+}$, which has been recently reported,[7] is of interest because it exhibits a spin equilibrium within a zeolite.

Experimental Section

Materials. A Linde Na–Y zeolite (Lot Number Y-52 3365-94) was used. 2,2′-Bipyridine and 2,2′,2″-terpyridine were purchased from K&K Laboratories and Sigma Chemical Co., respectively, and were used without further purification. Ultrapure grade oxygen from Matheson was further purified by passing it through a 4A sieve at 197 K. The sieve had previously been activated by heating under vacuum at 623 K for 2 h.

Table I. Summary of g Values and Hyperfine Coupling Constants for $[Co^{II}(terpy)_2]^{2+}$

anion or matrix	g_x	g_y	g_z	$A_x{}^a$	A_y	A_z	ref
zeolite	2.060	2.088	2.188	<30	15	75	this work
NO_3^-	2.034	2.132	2.207	<10	<10	~78	10
ClO_4^-	2.027	2.142	2.196	<10	<10	96	10

[a] Co hyperfine splitting; in gauss.

Preparation of $[Co^{II}(terpy)_2]^{2+}$ and $[Co^{II}(bpy)(terpy)]^{2+}$ Complexes in a Na–Y Zeolite. Two CoNa–Y zeolites with different cobalt contents were prepared from the Na–Y zeolite by exchange of Na^+ with Co^{2+} in 0.35 and 2.0 mM solutions of cobalt nitrate at 343 K for 24 H. The cobalt contents of the resulting zeolites were 4.1×10^{19} and 1.56×10^{20} Co^{2+} ions/g, as determined by atomic absorption. These values correspond to 1.2 and 4.5 cobalt ions per unit cell of zeolite or about 0.15 and 0.5 cobalt ion per large cavity. The two samples are referred to as $Co_{1.2}Na$–Y and $Co_{4.5}Na$–Y, respectively.

After they were mixed with predetermined amounts of bpy and terpy, the CoNa–Y zeolites were introduced into a Pyrex vessel (ca. 27-mL volume) with a quartz side arm for EPR measurements. The samples were outgassed at 298 K for 12 h, heated in a closed system at 473 K for 24 h, and finally heated under vacuum at 523 K for 24 h. To prepare the pure $[Co^{II}(terpy)_2]^{2+}$ complex, a mixture of $Co_{1.2}Na$–Y and terpy (Co:terpy = 1:2 mole ratio) was heated in an identical manner. Further heating under vacuum at temperatures up to 573 K and for periods up to 7 days did not increase the number of complexes that were formed.

EPR Spectral Measurements. The EPR spectra were recorded both at X-band (9.08 GHz) and at Q-band (35.7 GHz) frequences. The g values were determined relative to a 2,2′-diphenyl-1-picrylhydrazyl (DPPH) standard ($g = 2.0036$). Spin concentrations were calculated by numerical double intergration of the derivative spectra and comparison with the integrated spectrum of a phosphorus-doped silicon standard having a known spin concentration. The uncertainty in the spin concentration is estimated to be ±10%. Simulated EPR spectra were calculated by using the computer program SIM 13.[8]

Results and Discussion

$[Co^{II}(terpy)_2]^{2+}$. Terpyridine reacts with cobalt ions in a type-Y zeolite to form a low-spin complex that gives rise to the X-band EPR spectrum of Figure 1a and the Q-band spectrum of Figure 1c. The spectra, which are attributed to $[Co^{II}(terpy)_2]^{2+}$, are characterized by the g values and hyperfine coupling constants given in Table I. In this case, computer simulation of the X-band spectrum was not very effective since the program does not allow one to independently vary the line width for the three principal coordinates. The reported g values have been deduced mainly from the Q-band spectrum and the hyperfine splitting from both spectra. A similar spectrum (Figure 1b) was observed with $[Co^{II}(terpy)_2]Cl_2$ in frozen Me_2SO at 77 K. This complex was prepared

---

(1) Martell, A. E. *Acc. Chem. Res.* **1982**, *15*, 155.
(2) Vansant, E. F.; Lunsford, J. H. *Adv. Chem. Ser.* **1973**, *No. 121*, 441.
(3) Howe, R. F.; Lunsford, J. H. *J. Am. Chem. Soc.* **1975**, *97*, 5156.
(4) Howe, R. F.; Lunsford, J. H. *J. Phys. Chem.* **1975**, *79*, 1836.
(5) Davis, S. M.; Howe, R. F.; Lunsford, J. H. *J. Inorg. Nucl. Chem.* **1975**, *39*, 1069.
(6) Huchital, D. H.; Martell, A. E. *Inorg. Chem.* **1974**, *13*, 2966.
(7) Mizuno, K.; Lunsford, J. H. *Inorg. Chem.* **1983**, *22*, 3484.
(8) Lozos, G.; Hoffman, B.; Franz, B. *QCPE* **1974**, No. 265.

Table II. Summary of *g* Values and Hyperfine Coupling Constants for Five-Coordinate Cobalt Complexes

complex	temp, K	$g_\parallel$	$g_\perp$	$\lvert A_\parallel^{\mathrm{Co}}\rvert$[a]	$\lvert A_\perp^{\mathrm{Co}}\rvert$	$\lvert A_\parallel^{\mathrm{N}}\rvert$	ref
$[\mathrm{Co^{II}(bpy)(terpy)}]$-Y	77	2.012	2.250	101	~15	15	this work
	298	2.022	2.250	95	~15		this work
$[\mathrm{Co^{II}}((p\text{-}\mathrm{OCH_3})\mathrm{TPP})(\mathrm{py})]^{2+}$ [b]	77	2.025	2.327	84	11	16	12
$[\mathrm{Co^{II}(CH_3NC)_5}]$-Y	77	2.003	2.163	89	32		13

[a] In gauss. [b] $(p\text{-}\mathrm{OCH_3})$TPP = tetrakis(*p*-methoxyphenyl)porphyrin; py = pyridine.

Table III. Concentrations of Cobalt Complexes in CoNa–Y Zeolites

zeolite[a]	Co, Co(II)/g	$[\mathrm{Co^{II}(terpy)_2}]^{2+}$, spins/g	$[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$, spins/g	$[\mathrm{Co^{III}(bpy)(terpy)O_2^-}]^{2+}$, spins/g
$\mathrm{Co_{1.2}Na}$–Y	4.2×10^{19}	3.6×10^{18}	3.0×10^{18}	3.3×10^{18}
$\mathrm{Co_{4.5}Na}$–Y	16×10^{19}	4.4×10^{18}	5.6×10^{18}	5.3×10^{18}

[a] Co:bpy:terpy = 1:1:1 molar ratio.

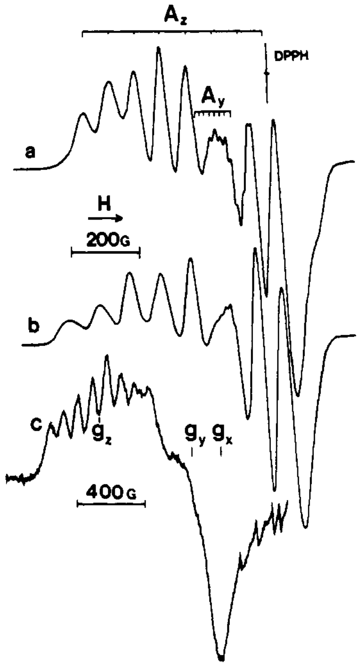

Figure 1. EPR spectra of $[\mathrm{Co^{II}(terpy)_2}]^{2+}$ complexes measured at 77 K: (a) X-band, in a $\mathrm{Co_{1.2}Na}$–Y zeolite; (b) X-band, in a frozen solution of $\mathrm{Me_2SO}$; (c) Q-band, in a $\mathrm{Co_{1.2}Na}$–Y zeolite.

in the manner described in the literature.[9]

Kremer et al.[10] have studied both low-spin and high-spin $[\mathrm{Co^{II}(terpy)_2}]\mathrm{X_2}\cdot n\mathrm{H_2O}$ complexes where X = $\mathrm{NO_3^-}$, $\mathrm{ClO_4^-}$ as well as other anions. Their EPR results are also reported in Table I. The orthorhombic symmetry indicated by the *g* values is consistent with the D_{2d} symmetry, which is expected from the two rigid tridentate ligands. Considerable variation in *g* values occurs when the ligands are either $\mathrm{NO_3^-}$ or $\mathrm{ClO_4^-}$, and it is not surprising that additional variations are noted when the zeolite is the anion.

The spin concentration of the complex in the $\mathrm{Co_{1.2}Na}$–Y zeolite was 1.7×10^{19} spins/g, which corresponds to 41% of the cobalt content. With the sample at 298 K, the spectrum, shown in Figure 1a, disappeared and a broad single line with $g \simeq 2.2$ and a width of 1450 G appeared. In view of the *g* value, this broad line is probably due to low-spin complexes having relatively short relaxation times. Although there is no direct evidence for high-spin complexes in the zeolite, their presence in $[\mathrm{Co^{II}(terpy)_2}]\mathrm{ClO_4\cdot 0.5H_2O}$[10] suggests that all or part of the remaining 59% of the cobalt in the zeolite may be the high-spin state.

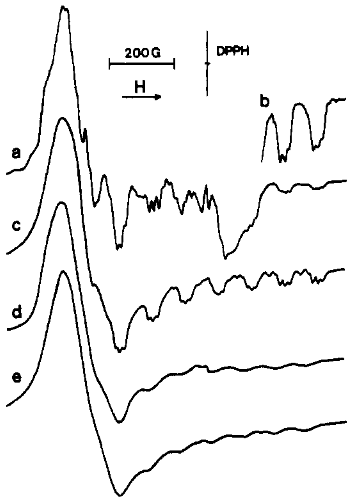

Figure 2. EPR spectra of $\mathrm{Co_{1.2}Na}$–Y zeolite after reaction with bipyridine–terpyridine mixture (Co:bpy:terpy = 1:1:1): (a) spectrum measured at 77 K; (b) spectrum amplified ×10; (c) simulated spectrum of (a), with only a $[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$ complex assumed; (d) spectrum measured at 298 K; (e) simulated spectrum of (d).

$[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$. A mixture of $\mathrm{Co_{1.2}Na}$–Y, bpy, and terpy (Co:bpy:terpy = 1:1:1 mole ratio) prepared in the manner described previously gave the EPR spectra depicted by curves a and d of Figure 2 when the sample was at 77 and 298 K, respectively. Spectra simulated by using the parameters given in Table II are shown by curves c and e. The *g* values and $^{59}\mathrm{Co}$ hyperfine constants are characteristic of a low-spin five-coordinate complex.[11,12] In the parallel components the presence of superhyperfine splitting due to $^{14}\mathrm{N}$ ($I = 1$) coordinated along the *z* axis also suggests a five-coordinate complex.[12] These spectra are attributed to the $[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$ complex in zeolite Y. Spin concentrations for the sample at 77 and 298 K were the same if one assumes a normal temperature effect on the EPR signal.

The spectrum recorded with the sample at 77 K is complicated by the overlapping spectrum of the $[\mathrm{Co^{II}(terpy)_2}]^{2+}$ complex. The presence of the latter complex is evident, in part, by comparing the simulated spectrum c with the actual specrum b in Figure 2. Upon admission of oxygen, the $[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$ complex formed the oxygen adduct (see below) but the $[\mathrm{Co^{II}(terpy)_2}]^{2+}$ complex remained unchanged. This is evident upon comparison of curves a and b of Figure

---

(9) Hogg, R.; Wilkins, R. G. *J. Chem. Soc.* **1962**, 341.

(10) Kremer, S.; Henke, W.; Reinen, D. *Inorg. Chem.* **1982**, *21*, 3013.

(11) Lunsford, J. H.; Vansant, E. F. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 1028.

(12) Walker, F. A. *J. Am. Chem. Soc.* **1970**, *92*, 4235.

(13) Lunsford, J. H.; Vansant, E. F. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 1028.

Table IV. Calculated Values of $A_{\mathrm{iso}}^{\mathrm{Co}}$, $A_{\mathrm{aniso}}^{\mathrm{Co}}$, and $\rho(4s)$ Five-Coordinate Cobalt Complexes

complex	temp, K	$A_{\mathrm{iso}}^{\mathrm{Co}}$, G	$A_{\mathrm{aniso}}^{\mathrm{Co}}$, G	$\rho(4s)$	$\rho(3dz^2)$
$[\mathrm{Co^{II}(bpy)(terpy)}]$-Y	77	−11	119	0.056	0.76
	298	−11	113	0.056	0.76
$[\mathrm{Co^{II}}(p\text{-}\mathrm{OCH_3TPP)(py)}]^{2+}$ [a]	77	−5	95	0.060	0.61
$[\mathrm{Co^{II}(CH_3NC)_5}]$-Y	77	−11	105	0.056	0.67

[a] (p-$\mathrm{OCH_3}$)TPP = tetrakis(p-methoxyphenyl)porphyrin; py = pyridine.

Table V. Magnetic Parameters of Oxygen Complexes in Zeolite Y

complex	g_x	g_y	g_z	$\lvert A_x \rvert$ [a]	$\lvert A_y \rvert$	$\lvert A_z \rvert$	ref
$[\mathrm{Co^{III}(bpy)(terpy)O_2^-}]^{2+}$	1.998	2.007	2.063	11.0	11.0	15.6	this work
$[\mathrm{Co^{III}(en)_2O_2^-}]^{2+}$ [b]	1.992	1.998	2.084	13	10	20	4
$[\mathrm{Co^{III}(NH_3)_5O_2^-}]^{2+}$	2.000	2.01	2.084	12.5	12	17.8	3
$[\mathrm{Co^{III}(CH_3NH_2)_5O_2^-}]^{2+}$	1.999	2.01	2.075	12.0	12	21	3
$[\mathrm{Co^{III}(PrNH_2)_5O_2^-}]^{2+}$ [c]	1.995	2.01	2.079	12.0	12	18.5	3

[a] Cobalt hyperfine splitting; in gauss. [b] en = ethylenediamine. [c] Pr = $\mathrm{CH_3CH_2CH_2}$.

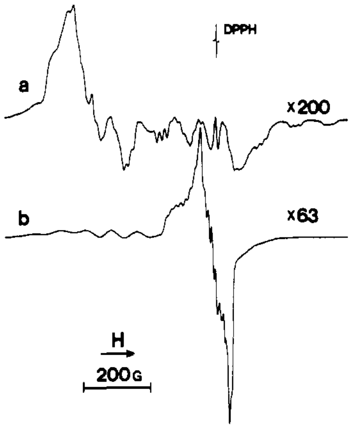

Figure 3. EPR spectra at 77 of $\mathrm{Co_{1.2}Na}$–Y zeolite after reaction with bipyridine–terpyridine mixture: (a) before exposure to $\mathrm{O_2}$; (b) after exposure to $\mathrm{O_2}$.

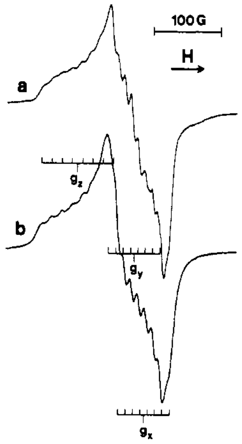

Figure 4. EPR spectra of $[\mathrm{Co^{III}(bpy)(terpy)O_2^-}]^{2+}$ complex: (a) experimental spectrum measured at 77 K; (b) simulated spectrum.

3. In curve b the spectrum of the $[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$ complex is no longer evident, and only the spectra of the unreacted $[\mathrm{Co^{II}(terpy)_2}]^{2+}$ and that of the oxygen adduct are present. The derivative spectra give a misleading impression of the relative amounts of the three complexes, and in fact, their concentrations, as determined from double integration, were approximately equal, as shown in Table III. In aqueous solution the stability constants (log K) for $[\mathrm{Co^{II}(terpy)_2}]^{2+}$, $[\mathrm{Co^{II}(bpy)_3}]^{2+}$, and $[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$ are 18.6, 15.9 and 14.88, respectively.[6,14] With the $\mathrm{Co_{1.2}Na}$–Y sample, 7% of the cobalt formed $[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$ complexes, but these were converted stoichiometrically to the oxygen adduct.

It is of interest to consider further the magnetic parameters of the $[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$ complex in the zeolite relative to other five-coordinate complexes. The expected ground state for these complexes is $(d_{xz,yz})^4(d_{xy})^2(d_{z^2})^1$, and for an unpaired electron in a d_{z^2} orbital $A_{\parallel}^{\mathrm{Co}} > 0$ and $A_{\perp}^{\mathrm{Co}} > 0$.[15] Moreover, the principal values of the g tensor are given by

$$g_{\parallel} \simeq g_e \qquad g_{\perp} = g_e + 6\lambda/\Delta \tag{1}$$

where $g_e = 2.0023$, λ is the spin–orbit parameter, and Δ is the energy between the $d_{xz,yz}$ and d_{z^2} orbitals. The hyperfine coupling constants are given approximately by[16]

$$A_{\perp} = A_{\mathrm{iso}}^{\mathrm{Co}} - \tfrac{1}{2}A_{\mathrm{aniso}}^{\mathrm{Co}}(1 - \tfrac{45}{12}\Delta g_{\perp}) \tag{2}$$

$$A_{\parallel} = A_{\mathrm{iso}}^{\mathrm{Co}} + A_{\mathrm{aniso}}^{\mathrm{Co}}(1 - \Delta g_{\perp}/4) \tag{3}$$

where $A_{\mathrm{iso}}^{\mathrm{Co}}$ and $A_{\mathrm{aniso}}^{\mathrm{Co}}$ are the isotropic and anisotropic hyperfine parameters in the absence of orbital magnetism and $\Delta g = g_{\perp} - g_e$. The $A_{\mathrm{iso}}^{\mathrm{Co}}$ and $A_{\mathrm{aniso}}^{\mathrm{Co}}$ values for the $[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$ complex are compared in Table IV with values obtained for related five-coordinate complexes.

In order to calculate the spin density on the Co(II) ion in the $3d_{z^2}$ orbital ($\rho(3d_{z^2})$), the calculated anisotropic hyperfine coupling constants ($A_{\mathrm{aniso}}^{\mathrm{Co}}$) are compared, with the theoretical value obtained for the odd spin being completely in the $3d_{z^2}$ orbital. In a similar manner, the spin density in the 4s orbital ($\rho(4s)$) can be calculated from[15]

$$A_{\mathrm{iso}}^{\mathrm{Co}} = [\rho(4s)]A_{\mathrm{iso}}^{\mathrm{Co}}(4s) + (1 - \rho(4s))A_{\mathrm{iso}}^{\mathrm{Co}}(3d\ (\text{spin polarization})) \tag{4}$$

where $A_{\mathrm{iso}}^{\mathrm{Co}}(4s) = 1320$ G and $A_{\mathrm{iso}}^{\mathrm{Co}}(3d\ (\text{spin polarization})) = -90$ G. The spin densities, $\rho(3d_{z^2})$ and $\rho(4s)$, for the several complexes are compared in Table IV. It is evident that the unpaired electron is highly localized in the $3d_{z^2}$ orbital. The remaining spin density is probably on the nitrogen, although without $A_{\perp}^{\mathrm{N}}$ it is not possible to determine the extent of this delocalization.

With such large ligands one must be concerned about the formation of the complex on the external surface of the zeolite crystallites, rather than in the large cavities. In order to explore this possibility, the zeolite containing $[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$ was slurried at 298 K with a benzene solution containing DPPH

---

(14) Martell, A. E.; Smith, R. M. "Critical Stability Constants"; Plenum Press: New York, 1982; Vol. 5.

(15) Symons, M. C. R.; Wilkinson, J. G. *J. Chem. Soc. A* **1971**, 2069.

(16) Griffith, J. S. *Discuss. Faraday Soc.* **1958**, *26*, 81.

(17) Tyuma, I.; Imai, K.; Shimizu, K. *Biochemistry* **1973**, *12*, 1491.

(18) Imai, K. *J. Biol. Chem.* **1974**, *249*, 7607.

(19) Ochiai, E. I. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1727.

at a sufficiently high concentration (10^{-1} M) so that spin exchange was apparent in the EPR spectrum. It should be noted that DPPH is sufficiently large that one would not expect it to diffuse into the zeolite cavities at room temperature. In the presence of the DPPPh solution, the EPR spectrum of the $[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$ complex remained unchanged, which indicates that the complex and the paramagnetic DPPH were not in close proximity to one another. Thus, we conclude that the cobalt complexes were present within the zeolite cavities and not primarily on the external surface.

$[\mathrm{Co^{III}(bpy)(terpy)O_2^-}]^{2+}$. The $[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$ complex reacted rapidly and stoichiometrically with 30 torr of O_2 to form a new complex that is characterized by the EPR spectra of Figures 3b and 4a. The magnetic parameters for this complex and those of other complexes of the type $[\mathrm{Co^{III}L_xO_2^-}]^{2+}$ in zeolite Y are compared in Table V.[2-4] The agreement indicates that the $[\mathrm{Co^{III}(bpy)(terpy)O_2^-}]^{2+}$ complex was indeed formed. The experimental spectrum (Figure 4a) was best simulated (Figure 4b) by assuming three sets of eight hyperfine lines due to ^{59}Co. This suggests a bent structure for the superoxide ion. The small values for the ^{59}Co hyperfine constants confirm that the unpaired electron is mainly localized on the dioxygen moiety.

In an attempt to increase the fraction of Co(II) that was converted to $[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$ and the corresponding oxygen adduct, both the temperature of complex formation and the amount of ligands were varied. A mixture of $\mathrm{Co_{1.2}Na}$–Y with bpy and terpy (Co:bpy:terpy = 1:1:1) was heated progressively from 470 to 550 K. At intervals, O_2 was added at 298 K to the sample and the spin concentration of the oxygen adduct was determined. The concentration of the adduct increased for higher reaction temperatures up to 520 K, but from 520 to 550 K no additional complexes were formed. The maximum concentration of superoxide ions was ca. 8% of the total cobalt. Likewise, Co to ligand ratios of Co:bpy:terpy = 1:1:2 and 1:2:1 yielded smaller amounts of the oxygen adduct.

Equilibration of the complex in the zeolite with oxygen required less than 1 min at 298 K as determined by the pressure change in the gas phase. The concentration of the superoxide ion was independent of the oxygen pressure in the range 15–50 torr, although line broadening of the signal due to interaction of the complex with paramagnetic oxygen molecules was observed at pressures above 35 torr. Spin concentrations were the same with the sample at 77 and 298 K. On brief evacuation (10 s) at 298 K, the concentration of the superoxide ion decreased to 20% of the original value. No spectrum of the oxygen adduct was detected after evacuation of the gas phase for 5 min, and the spectrum of the $[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$ complex reappeared. At 298 K this phenomenon was reversible many times.

Although the reversible formation and decomposition of the oxygen adduct is rapid, the complex is rather stable when compared with similar mononuclear complexes. From an evaluation of $P_{1/2}$, the O_2 pressure at half-oxygenation, a stability constant of $K_{O_2} = 1.7$ torr^{-1} at 298 K was determined. This may be compared with K_{O_2} values of 0.53 torr^{-1} for human hemoglobin A at 298 K in H_2O and 0.0030 torr^{-1} for $\mathrm{Co(salen)}^{2+}$ (salen = 1,6-bis(2-hydroxyphenyl)-2,5-diaza-1,5-hexadiene) at 293 K in $\mathrm{Me_2SO}$. The unusually large stability constant in the zeolite may result, in part, from the fact that K_{O_2} is determined from the gas-phase pressure, not the actual concentration of O_2 in the solvent. In water, for example, the concentration of O_2 is considerably less than the concentration of O_2 in the gas phase at the same pressure, but in the zeolite the O_2 concentration at 298 K is essentially that of the gas phase. Moreover, during the formation of the complex the solvent may have to be displaced from the coordination site on the metal ion, but in the zeolite the oxygen framework does not interfere with the formation of the oxygen adduct.

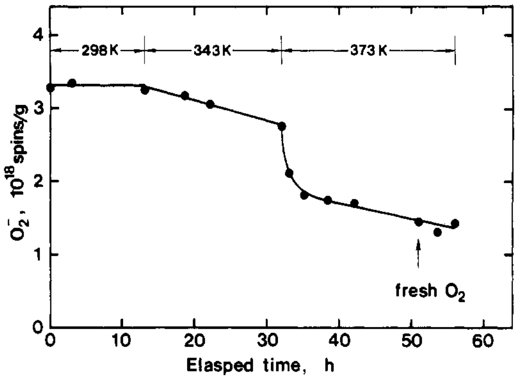

Figure 5. Stability of $[\mathrm{Co^{III}(bpy)(terpy)O_2^-}]^{2+}$ complex in the presence of O_2 as a function of time at 298, 343, and 373 K.

A situation more comparable to that of conventional solvents occurs when water is adsorbed into the zeolite. Equilibration of the zeolite with 20 torr of water for 7 h at 298 K totally prevented the formation of the superoxide ion. Following adsorption of water, but prior to addition of O_2, the spectrum of the $[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$ complex was not observed, and only the spectrum of a small amount of $[\mathrm{Co^{II}(terpy)_2}]^{2+}$ was detected. The effect of water on the $[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$ complex was partially reversed upon heating the sample under vacuum at 423 K and was completely reversed upon heating the sample under vacuum at 523 K. These phenomena suggests that water coordinates to $[\mathrm{Co^{II}(bpy)(terpy)}]^{2+}$ more strongly than oxygen and that the complex is in a high-spin state when water is present in the zeolite. Our recent study of the spin equilibrium for $[\mathrm{Co^{II}(bpy)_3}]^{2+}$ demonstrated that the low-spin complex was much more strongly favored in a dehydrated zeolite that in frozen $\mathrm{Me_2SO}$.[7] This inhibition by water, together with the propensity to form dinuclear complexes,[6] may explain why $[\mathrm{Co^{II}(bpy)(terpy)O_2^-}]^{2+}$ complexes have not been observed in aqueous systems.

The stability of the superoxide ion toward reaction with the bpy and terpy ligands was investigated by heating the sample in the presence of oxygen as indicated in Figure 5. No change in the spin concentration was observed at 298 K over a period of 12 h. In a separate experiment, a similar sample was kept in the presence of oxygen at 298 K for 10 days and no change in the EPR spectrum was detected. The results of Figure 5 show that a slow decrease in the EPR signal occurred when the sample was heated to 343 K, and a more rapid decrease was observed at 373 K. The sample was briefly evacuated at 298 K and 30 torr of fresh oxygen was added, but no increase in the signal was noted. After this stability test, the sample was evacuated again at 523 K for 16 h and then exposed to 30 torr of oxygen at 298 K. The concentration of the oxygen adduct increased to about 60% of the original value. These results suggest that the complexed oxygen reacts with the ligands to form one or more compounds that block the sixth coordination site. The reversible effect may be due to the formation of water, but it is evident from the results that an even more strongly coordinated species must be responsible for the irreversible reaction. The formation of dinuclear complexes is unlikely because (a) there is insufficient volume to have all of the ligands in one cavity and (b) if mononuclear complexes existed in adjacent cavities the distance between metal ions would be too great to accomodate briding oxygens.

This system appears to have potential as a practical means of removing oxygen from dry air because of its stability with respect to cycling at 298 K. The rapid formation and decomposition of the oxygen adduct is also attractive. One problem, however, is the low density of the complexes, which means that very large volumes of the zeolite would have to be used. In principle, it should be possible to form a complex in every large cavity of the zeolite.

Acknowledgment. We are grateful to Dr A. E. Martell for bringing to our attention the mixed-ligand bipyridine-terpyridine complex of cobalt. The Q-band EPR spectrum was kindly obtained by Dr. W. S. Millman at the University of Wisconsin-Milwaukee. This work was supported by the U.S. Army Research Office.

Registry No. $[Co^{II}(terpy)_2]^{2+}$, 18308-16-2; $[Co^{II}(bpy)(terpy)]^{2+}$, 52225-38-4; $[Co^{III}(bpy)(terpy)O_2^-]^{2+}$, 91743-35-0.

Contribution from the Department of Chemistry,
University of Queensland, Brisbane, Australia 4067

Reactions of Platinum(II) Aqua Complexes. 1. Multinuclear (^{195}Pt, ^{15}N, and ^{31}P) NMR Study of Reactions between the *cis*-Diamminediaquaplatinum(II) Cation and the Oxygen-Donor Ligands Hydroxide, Perchlorate, Nitrate, Sulfate, Phosphate, and Acetate[1]

TREVOR G. APPLETON, RON D. BERRY, CAROL A. DAVIS, JOHN R. HALL,* and HEATHER A. KIMLIN

Received November 28, 1983

Reactions in aqueous solution between *cis*-$[Pt(^{15}NH_3)_2(H_2O)_2](ClO_4)_2$ and anions A^{m-} (ClO_4^-, OH^-, NO_3^-, SO_4^{2-}, $H_2PO_4^-$, $CH_3CO_2^-$) have been studied with use of ^{195}Pt, ^{15}N, and, for phosphate, ^{31}P NMR. The monohydroxo-bridged complex $(Pt(NH_3)_2(H_2O))_2(\mu\text{-}OH)^{3+}$ has been obtained in solution by reaction of $[Pt(NH_3)_2(\mu\text{-}OH)]_n^{n+}$ with acid or as an intermediate in the formation of these oligomers from *cis*-$Pt(NH_3)_2(OH)(H_2O)^+$. Perchlorate does not coordinate. Nitrate and sulfate each gives a complex *cis*-$Pt(NH_3)_2(A)(H_2O)^{(2-m)+}$, with A^{m-} unidentate. In acidic solution (pH 1.5), phosphate gives only *cis*-$Pt(NH_3)_2(OPO_3H_2)(H_2O)^+$. When deprotonated, this complex is in equilibrium with $(Pt(NH_3)_2)_2(\mu\text{-}OH)(\mu\text{-}PO_4H)^+$ and other complexes containing bridging phosphate. Reaction with oxygen gives blue solids and solutions. Analogous phosphate complexes are formed with methylamine and ethylenediamine, although blue solutions with methylamine are obtained only after prolonged exposure to light. In solution, acetate gives *cis*-$Pt(NH_3)_2(O_2CCH_3)(H_2O)^+$, and $Pt(NH_3)_2(O_2CCH_3)_2$, with smaller amounts of $(Pt(NH_3)_2)_2(\mu\text{-}OH)(\mu\text{-}O_2CCH_3)^{2+}$. With perchlorate, a solid $[Pt(NH_3)_2(O_2CCH_3)]ClO_4{\cdot}H_2O$ crystallizes, which probably contains bridging acetate. Solutions turn blue-black when heated, indicating that oligomers with mixed oxidation states of platinum form. Solid *cis*-$Pt(NH_3)_2(O_2CCH_3)_2{\cdot}2H_2O$ may be isolated. It is quite soluble in water.

Introduction

There has been considerable interest in platinum(II) amine complexes since the discovery that *cis*-$Pt(NH_3)_2Cl_2$ and a number of analogues possess antitumor activity.[2] Many syntheses, including the now standard Dhara method for preparing the compounds *cis*-$Pt(NH_2R)_2Cl_2$,[3] use the aqua complexes *cis*-$Pt(NH_2R)_2(H_2O)_2^{2+}$ as intermediates. Despite this, relatively little is known of the solution chemistry of the aqua complexes, including the extent of reaction with the weakly coordinating counterions usually present (reaction 1).

$$cis\text{-}Pt(NH_2R)_2(H_2O)_2^{2+} + A^{m-} \rightleftharpoons Pt(NH_2R)_2(A)(H_2O)^{(2-m)+} + H_2O \quad (1)$$

When ^{15}N-substituted ammonia is used, ^{195}Pt and ^{15}N NMR can be very useful in investigating reactions of *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$.[4-7] In this work, NMR spectroscopy with these nuclei has been used to study reactions 1.

We have previously shown[8] that a number of the complexes *cis*-$Pt(NH_2R)_2(H_2O)_2^{2+}$ rapidly give blue solutions and solids when mixed with phosphate and exposed to air. We have used ^{31}P NMR in conjunction with ^{195}Pt and ^{15}N NMR to examine these solutions. While this paper was in preparation, a report appeared giving some preliminary ^{195}Pt and ^{31}P data on similar solutions, but no attempt was made to assign the resonances to specific complexes.[9]

Experimental Section

Instruments and Techniques. NMR spectra at 10.1 MHz (^{15}N), 21.4 MHz (^{195}Pt), 25 MHz (^{13}C), and 40.3 MHz (^{31}P) were obtained with a JEOL FX-100 instrument, with a tunable 10-mm multinuclear probe, at 28 °C. ^{15}N spectra were run at 2000 Hz width, typically by using 2000 scans, with 3 s between 10-μs pulses (22° tilt). Shifts are relative to the $^{15}NH_4^+$ signal from 5 M $^{15}NH_4{}^{15}NO_3$ in 2 M HNO_3 contained in a coaxial capillary.[10] ^{195}Pt spectra were obtained typically with spectrum width 20 or 10 KHz, 1000-3000 scans, total delay 0.3-0.5 s between 20-μs pulses (70 tilt), and a separate aqueous solution of Na_2PtCl_6 as reference.[11] ^{31}P spectra were obtained with use of 10-KHz scans, 100 10-μs pulses at 1-s intervals (27° tilt). Spectra were initially referenced relative to free phosphate in the solutions and then adjusted relative to external 85% H_3PO_4 following calibration of the shift of free phosphate in solution as a function of pH. Below pH 3, there was no significant difference between the shifts. All these

---

[1] Presented in part as a poster at the 11th Conference of the Coordination and Metal-Organic Division of the Royal Australian Chemical Institute, August 1982, Canberra, Australia.

[2] Rosenberg, B.; Van Camp, L.; Trosko, J. R.; Mansour, V. H. *Nature (London)* **1969**, *222*, 385.

[3] Dhara, S. C. *Indian J. Chem.* **1970**, *8*, 193.

[4] Rosenberg, B. *Biochimie* **1978**, *60*, 859.

[5] Boreham, C. J.; Broomhead, J. A.; Fairlie, D. P. *Aust. J. Chem.* **1981**, *34*, 659.

[6] Chikuma, M.; Pollock, R. J. *J. Magn. Reson.* **1982**, *47*, 324.

[7] Alei, M.; Vergamini, P. J.; Wageman, W. E. *J. Am. Chem. Soc.* **1979**, *101*, 5415.

[8] Appleton, T. G.; Berry, R. D.; Hall, J. R. *Inorg. Chim. Acta* **1982**, *64*, L229.

[9] Wood, F. E.; Hunt, C. T.; Balch, A. L. *Inorg. Chim. Acta* **1982**, *67*, L19.

[10] Jones, A. J.; McNab, H.; Hanisch, P. *Aust. J. Chem.* **1978**, *31*, 1005.

[11] Kerrison, S. J. S.; Sadler, P. J. *J. Magn. Reson.* **1977**, *31*, 321.